



**EDGEWOOD**

RESEARCH, DEVELOPMENT & ENGINEERING CENTER

U.S. ARMY CHEMICAL AND BIOLOGICAL DEFENSE COMMAND

ERDEC-CR-236

**ANALYSIS AND DESIGN  
OF THE ADSORBENT SAMPLE TEMPERATURE CONTROL  
IN THE VOLUMETRIC ISOTHERM SYSTEM**

David T. Croft  
Scott M. Maurer  
David L. Fowler

GUILD ASSOCIATES, INC.  
Baltimore, MD 21236

19971117 087

September 1997

Approved for public release; distribution is unlimited.



Guild  
Associates, Inc.



Aberdeen Proving Ground, MD 21010-5423

#### **Disclaimer**

**The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.**

<b>REPORT DOCUMENTATION PAGE</b>			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE September 1997		3. REPORT TYPE AND DATES COVERED Final - 95 Oct - 95 Dec
4. TITLE AND SUBTITLE Analysis and Design of the Adsorbent Sample Temperature Control in the Volumetric Isotherm System			5. FUNDING NUMBERS  C-DAAM01-96-C-0043	
6. AUTHOR(S) Croft, David T., Maurer, Scott M., and Fowler, David L.				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Guild Associates, Inc., 5022 Campbell Boulevard, Baltimore, MD 21236			8. PERFORMING ORGANIZATION REPORT NUMBER  ERDEC-CR-236	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)  DIR, ERDEC, ATTN: SCBRD-RT/ASM, APG, MD 21010-5423			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES COR: David Reed, SCBRD-RT/ASM, (410) 671-8212				
12a. DISTRIBUTION/AVAILABILITY STATEMENT  Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  The propagation of error in the volumetric isotherm apparatus used at Guild Associates, Inc. is discussed as well as modifications to the apparatus to reduce errors. Investigators found that errors in temperature measurement and/or control may affect vapor-phase and adsorbed-phase concentrations in a complex but predictable manner. Changes to the isotherm apparatus to increase the accuracy of temperature measurements and improve the stability of the temperature control are documented.				
14. SUBJECT TERMS  Adsorption isotherm measurement			15. NUMBER OF PAGES  24	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT <b>UNCLASSIFIED</b>	18. SECURITY CLASSIFICATION OF THIS PAGE <b>UNCLASSIFIED</b>	19. SECURITY CLASSIFICATION OF ABSTRACT <b>UNCLASSIFIED</b>	20. LIMITATION OF ABSTRACT  <b>UL</b>	

Blank

## PREFACE

The work described in this report was authorized under Contract No. DAAM01-96-C-0043. This work was started October 1995 and completed December 1995.

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for public release. Registered users should request additional copies from the Defense Technical Information Center; unregistered users should direct such requests to the National Technical Information Service.

Blank

## CONTENTS

1.	INTRODUCTION.....	7
2.	THEORY .....	8
2.1	Propagation of Temperature Errors.....	8
2.2	Equation to Determine the Length of Heat Exchanger Section.....	12
3.	SAMPLE TEMPERATURE CONTROL APPARATUS.....	12
3.1	Glass Jacket.....	12
3.2	Copper Jacket.....	13
3.3	Horizontal or Vertical Orientation.....	13
4.	ANALYSIS.....	13
4.1	In the Absence of Temperature Gradients .....	14
4.2	Temperature Gradients and Temperature Control .....	14
5.	MODIFICATIONS MADE.....	16
5.1	Changes to Heat Exchanger Length.....	16
5.2	Changes Made to Reduce Axial Temperature Gradients.....	16
5.3	Stability to Flow Disturbances.....	16
6.	TESTING MODIFICATIONS .....	17
6.1	Measured Temperature Gradients Across the Sample Container.....	17
6.2	Importance of Heat Conductor-Exchanger and Heat Conductor.....	17
6.3	Measured Temperature Response to Flow Disturbance.....	18
7.	DISCUSSION.....	19
8.	CONCLUSION.....	20

## FIGURES

1	Volumetric Isotherm System Schematic.....	21
2	a) Old Temperature Control System and b) Old Adsorption Bed Schematics ..	22
3	a) Temperature Control Jacket and b) Adsorption Bed Assembly Schematics .....	23
4	Temperature Gradient Across Adsorbent Sample Container.....	24

## TABLES

1	Percent error in $p$ per error of 1 C (R-134a/BPL).....	11
2	Percent error in $p$ per error of 1 C (Toluene/BPL) .....	11
3	Physical properties of Air and He.....	14
4	Percent error in $p$ per standard deviation of T with vertical copper (R-134a/BPL) .....	18
5	Percent error in $p$ per standard deviation of T with vertical copper (Toluene/BPL) .....	19



# ANALYSIS AND DESIGN OF THE ADSORBENT SAMPLE TEMPERATURE CONTROL IN THE VOLUMETRIC ISOTHERM SYSTEM

## 1. INTRODUCTION

An adsorption equilibrium datum consists of an adsorbed-phase concentration, a vapor-phase concentration (or partial pressure) and a temperature. Specifying any two of these thermodynamic variables fixes the third. In order to measure an adsorption isotherm, the temperature is fixed and the adsorbed-phase concentrations corresponding to a series of vapor-phase concentrations are determined. Limitations on the precision and accuracy of analytical equipment such as a flame ionization detector (FID), gas chromatograph, integrator, thermocouples and signal processing modules introduce measurement errors. Other sources of error may be due to unanticipated concentration or temperature gradients within the isotherm system. Limitations on the effectiveness of temperature control is also a possible source of error. Knowing the limitations of various pieces of equipment and being aware of uneven concentration and temperature distributions is important when it comes to estimating the error in an isotherm measurement. It is also necessary and important to understand how errors in measuring or controlling one of three thermodynamic variables affects the others.

The heart of the volumetric isotherm measurement system is the bypass loop and the challenge loop shown in Figure 1. The bypass loop consists of a ballast of known volume, a compressor or pump, and connecting tubing. The challenge loop includes connecting tubing, the ballast (either 1, 4 or 6 liters of volume), the pump (either a Ruska or Metal Bellows MB41 pumps) and the adsorbent sample container. The adsorbent sample container is surrounded by a temperature controlled jacket. In the bypass mode, adsorbate is injected into the bypass loop, pumped around the loop until it is well mixed, then a small sample (1 ml) is removed and analyzed to obtain a vapor-phase concentration. Since the volume of the bypass loop is known, the mass injected may be calculated. The system is then switched to challenge mode where adsorption is allowed to occur. Vapor is circulated through the challenge loop until adsorption equilibrium is achieved. The vapor-phase concentration is again measured and the adsorbed-phase concentration is calculated using the mass of chemical last lost from the vapor phase.

The system ballast and the sample container assembly are usually not at the same temperatures. In challenge mode, gas within the system is pumped from the ballast, which is typically at or near room temperature, to the sample container heat exchange assembly, where it is brought to the isotherm temperature. When the gas leaves the jacketed region it returns to the ballast temperature.

The *actual* vapor-phase concentration, adsorbed-phase concentration and temperature are related in one way and the *measured* values of these quantities are related in another. The actual distribution of adsorbate between adsorbed and vapor-phases depends on temperature. When adsorption is highly favorable, a change in temperature may have only a small effect on the actual adsorbed-phase concentration within the challenge loop when equilibrium is reestablished. The same temperature change, however, may cause a significant shift in the vapor-phase concentration. Because the adsorbed-phase concentration is calculated from a mass balance based on vapor-phase measurements, large changes in the gas-phase concentration lead to large changes in the calculated adsorbed-phase concentration. Errors in temperature measurements or temperature control affect the reliability not only of temperature measurements but of vapor-phase and adsorbed-phase concentration measurements as well.

The affect temperature errors have on measurements of adsorbed-phase concentrations may be significant, especially for strongly adsorbed substances. The report analyzes this effect. It also documents improvements made in temperature measurement and temperature control of the adsorbent in the volumetric system at Guild Associates, Inc.

## 2. THEORY

Because both adsorbed-phase and vapor-phase concentrations are determined from measurements made on the vapor phase, determining the effect an error in the temperature has on the vapor-phase concentration will also indicate the error introduced into the adsorbed-phase concentration measurement. Temperature errors may be due to thermal gradients or differences between the adsorbent and the surrounding gas. The theory section treats error propagation. There is also a section on heat exchange.

### 2.1 Propagation of Temperature Errors.

In order to assess the error due to inaccurate temperature measurements and/or poor temperature control, the derivative of the vapor-phase adsorbate partial pressure (which is easily related to concentration) with respect to the temperature may be determined. This derivative can then be multiplied by the error in temperature measurement in order to estimate the error in the concentration (or partial pressure) determinations. The total number of moles of the adsorbate remains constant during the challenge mode vapor-phase concentration determination. The derivative which needs to be determined is therefore the change in adsorbate partial pressure with respect to temperature with the total number of moles in the system held constant. It is required to determine

$$\Delta p = \left( \frac{\partial p}{\partial T} \right)_{k_1} \Delta T \quad (1)$$

where

$$k_1 = q + \frac{pV_s}{m_a RT} \quad (2)$$

The adsorbate partial pressure is denoted by  $p$  and the temperature by  $T$ ,  $k_1$  represents the constant total adsorbate mass in the system defined on a per adsorbent mass basis and is defined in Eq. 2. The first term on the right side of Eq. 2 is proportional to the amount of adsorbate in the adsorbed phase and the second term is proportional to the amount in the vapor phase. In Eq. 2,  $q$  is the adsorbed-phase concentration. The vapor-phase concentration is  $p/RT$ . The system volume is  $V_s$  and the weight of the adsorbent is  $m_a$ . In order to determine the partial derivative in Eq. 1, the total differential is written and then is solved for the derivative of Eq. 1 subject to Eq. 2.

$$dp = \left( \frac{\partial p}{\partial T} \right)_q dT + \left( \frac{\partial p}{\partial q} \right)_T dq \quad (3)$$

Solving for  $dq$  using Eq. 2, we have  $dq = - (V_s/m_a RT) dp$  and

$$\left( \frac{\partial p}{\partial T} \right)_{k_1} = \frac{(\partial p / \partial T)_q}{1 + \frac{V_s}{m_a RT} \left( \frac{\partial p}{\partial q} \right)_T} \quad (4)$$

The first term on the right of Eq. 4 is the change in partial pressure with temperature holding the adsorbed-phase concentration  $q$  constant. This is divided by a factor which corrects for the fact that it is the total amount in the system that is kept constant rather than the adsorbed-phase concentration.

The extent to which an error in a temperature measurement can result in an error in *measured* adsorption equilibrium may be considered to depend on the enthalpy of adsorption. The enthalpy of adsorption can be related to the adsorption equilibria by

$$\lambda = RT^2 \left( \frac{\partial \ln p}{\partial T} \right)_q \quad (5)$$

where  $\lambda$  is the enthalpy of adsorption,  $R$  is the gas constant,  $T$  is the temperature,  $p$  is the adsorbate partial pressure, and  $q$  is the adsorbed phase concentration (also called loading). The partial derivative of Eq. 5 is taken holding the adsorbed-phase concentration  $q$

constant. Defining  $\left(\frac{\partial p}{\partial T}\right)_q$  of Eq. 4 in terms of the enthalpy of adsorption using Eq. 5 we have

$$\left(\frac{\partial p}{\partial T}\right)_{k_1} = \left[ \frac{p\lambda}{RT^2} \right] \left[ \frac{1}{1 + \frac{V_s}{m_a RT} \left(\frac{\partial p}{\partial q}\right)_T} \right] \quad (6)$$

The enthalpy of adsorption  $\lambda$  and the derivative  $\left(\frac{\partial p}{\partial q}\right)_T$  for a given adsorbate/adsorbent system can be estimated from experimental adsorption isotherms. This may be done by first fitting data measured at several temperatures to an isotherm equation with a temperature dependence and then evaluating the required derivatives. The Dubinin-Radushkevich (D-R) equation used with the Antoine equation may be used for this purpose. In terms of the D-R and Antoine equations, the enthalpy of adsorption is defined by

$$\lambda = \frac{BRT^2}{(C + T)^2} + \beta E [-\ln \theta]^{1/2} \quad (7)$$

and the partial of the partial pressure with respect to adsorbed-phase concentration holding temperature constant is

$$\left(\frac{\partial p}{\partial q}\right)_T = \frac{\beta E}{2RT} \frac{p}{q} [-\ln \theta]^{-1/2} \quad (8)$$

For determination of the change in adsorbed-phase concentration the equation for temperature error propagation is

$$\Delta q = \frac{V_s}{m_a} [p_b - (p_c + \Delta p_c)] \quad (9)$$

where the subscript  $b$  is for bypass mode and the subscript  $c$  is for challenge mode, both at equilibrium. Note that errors in the adsorbed-phase determination accumulate. Errors occurring in the first calculation are carried over to the second and so on.

Results obtained applying Eq. 1 are shown in Table 1 and Table 2. In order to get a percent error in  $p$  both sides of Eq. 1 were divided by  $p$  and multiplied by 100%. The system volume was assumed to be 3 liters and the mass of the adsorbent was

assumed to be 0.25 grams. The R-134a and toluene values of  $q^{sat}$  and  $\beta E/R$  were obtained from using the correlation reported in Croft.<sup>1</sup>

**TABLE 1. Percent error in  $p$  per error of 1 C (R-134a/BPL)**

T	$\theta = 0.5$	$\theta = 0.1$	$\theta = 0.01$	$\theta = 0.001$	$\theta = 0.0001$
25C	0.12%	2.16%	5.54%	7.15%	8.07%
50C	0.04%	0.72%	2.57%	3.81%	4.29%
150C	0.00%	0.02%	0.04%	0.04%	0.03%

**TABLE 2. Percent error in  $p$  per error of 1 C (Toluene/BPL)**

T	$\theta = 0.5$	$\theta = 0.1$	$\theta = 0.01$	$\theta = 0.001$	$\theta = 0.0001$
25C	7.66%	10.01%	12.02%	13.57%	14.87%
50C	5.92%	8.40%	10.11%	11.43%	12.53%
150C	0.41%	3.87%	5.59%	6.43%	7.09%

Tables 1 and 2 indicate that percent errors tend to increase as adsorbed-phase concentration decreases. For R-134a at 150 C the errors begin to decrease with decreasing adsorbed-phase concentration at adsorbed-phase concentrations below  $\theta = 0.001$ . Errors decrease with increasing temperature and are larger for more strongly adsorbed vapors such as toluene than for more weakly adsorbed vapors such as R-134a.

Small errors in temperature measurement or control may translate into much larger errors in partial pressures and, through Eq. 9, the corresponding calculated adsorbed-phase concentrations. A 1% error in a temperature measurement at 298 K is about 3 K. This may translate into more than a 30% error in the partial pressure for toluene when  $\theta = 0.01$ . Because of the method used to determine the adsorbed-phase concentration, a 30% error may result. In addition, these errors may accumulate from isotherm point to isotherm point. Errors in temperature measurement or control could thus result in concentration errors more than an order of magnitude greater. A temperature error of 1 % may introduce three times as much total error than a 10 % error in the GC calibration or a system volume determination. Precise temperature measurement and control is vitally important.

<sup>1</sup> Croft, D.T., Chemical Demilitarization Incinerator Post-Treatment Filter Modeling Fundamentals, U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD, unpublished data.

## 2.2 Equation to Determine The Length of Heat Exchanger Section.

For an idealized system, where everything within the jacketed region is maintained at the set-point temperature, the length of tubing that is required to bring the gaseous fluid to temperature can be estimated using Eq. 16 from Chapter 12, McCabe, et al.,<sup>2</sup> which is:

$$\frac{T_w - T_b}{T_w - T_a} = 0.81904e^{-3.657\pi/Gz} + 0.09760e^{-22.31\pi/Gz} + \dots \quad (10)$$

where  $T_w$  is the temperature of the tube wall,  $T_a$  is the temperature of the gas at the inlet, and  $T_b$  is the cross sectional averaged temperature at the tube outlet.  $Gz$  is the Graetz number and is defined

$$Gz = \frac{\rho Q c_p}{k L} \quad (11)$$

where  $\rho$  is the fluid density,  $Q$  is the volumetric flow rate,  $c_p$  is the heat capacity,  $k$  is the thermal conductivity and  $L$  is the length of tubing.

## 3. SAMPLE TEMPERATURE CONTROL APPARATUS

The adsorbent temperature control jacket is a critical feature of the volumetric isotherm system. It not only maintains the adsorbent at the isotherm temperature, but with the sample container assembly constitutes the heat exchanger that brings vapor to the isotherm temperature. Two such temperature control jacket-sample container systems are described below.

### 3.1 Glass Jacket.

The first temperature control and heat exchanger adsorbent sample container assembly is shown in Figure 2. It consists of a 1" OD glass sleeve wrapped with a heating tape. This is surrounded by a glass water jacket with 1-1/2" ID and a 2-1/2" OD. The glass sleeve is about 20" long and the water jacket is about 18" long. The glass jacket is wrapped with rock-wool insulation. The adsorption bed assembly (Figure 2b) has a leading 1/8" stainless steel tube (Tube A) which is coiled for heat exchange. The sample container is made from 3/8" stainless steel tubing and is approximately 3" long. It is followed by a length of 1/8" tubing extending out of the glass sleeve.

---

<sup>2</sup>Mccabe, W.L., Smith, J.C., and Harriott, P., Unit Operations of Chemical Engineering, 4th ed., McGraw-Hill, Incorporated, New York, NY, 1985.

### 3.2 Copper Jacket.

Figure 3 shows the second temperature control jacket and heat exchanger adsorbent sample container assembly. The temperature control jacket (Figure 3a) consists of a heat conducting sleeve 24" long. The sleeve is made from two concentric copper pipes. The inner pipe having a 3/4" OD has aluminum foil wrapped around it so as to allow it to snugly fit into the outer 1" OD copper pipe. The copper sleeve is wrapped with 3/8" copper tubing through which cooling (or heating) water may flow. Heating tape is wrapped around the layer of water coils and this is encased in rock-wool insulation 26" in length. The rock-wool, which is a brittle material, is sealed on the inside and at the top and bottom with temperature resistant tape rated to temperatures up to 250 C. The rock-wool is held in place with duct tape wrapped around the outside of the jacket. The adsorption bed assembly (Figure 3b) consists of a straight section of 1/8" stainless steel tubing (Tube A). The carrier gas is then directed to a heat conductor-exchanger (identical to the sample container). There is then another section of 1/8" stainless steel tube (Tube B) followed by the sample container (Adsorbent Bed). There is another section of 1/8" tube. Wrapped around Tube C is a heat conductor made of aluminum foil.

### 3.3 Horizontal or Vertical Orientation.

The two systems shown above are vertically oriented. A third configuration which will be discussed briefly is essentially the copper jacketed system oriented horizontally rather than vertically.

## 4. ANALYSIS

At any given time most of the gas within the apparatus is at or near room temperature. Only as gas is forced through the temperature controlled jacketed region is it heated or cooled. Not only does the sample container need to be maintained at a constant known temperature, but the vapor entering the jacketed region at room temperature must be brought to the temperature at which the isotherm is being measured. The flow rates through the challenge circuit depends on the position of the needle valve and on the pump used. Using the current system hardware, flow rates can range from 0.25 (using the Ruska pump) to 4 SLPM (using the Metal Bellows pump). For a 1/8" tube the corresponding range of Reynolds numbers is 170 to 2800. These Reynolds numbers span the laminar range up to the transitional range. The heat transfer area required to meet the set-point temperature throughout this flow rate range must be determined.

#### 4.1 In the Absence of Temperature Gradients.

The following calculation applies to an idealized heat exchanger where the temperature of the leading tube wall is constant. Laminar flow is assumed as a worst case because transitional turbulence aids in heat transfer. To determine the minimum length of tubing required to change the temperature of in-coming vapor from  $T_a = 298.2$  K to  $T_b = 398.1$  K, where  $T_w = 398.2$  K, Eq. 10 is truncated after the first term right of the equal sign and solved for the Graetz number of 1.71. For  $Gz = 1.71$ , the contribution of the second term right of the equal sign is negligible and therefore truncating the equation is justified.

The system may be operated using air or helium (relevant nitrogen physical properties are essentially equal to those of air) as an inert. Physical properties needed to solve for  $L$  of Eq. 11 are shown in Table 3. The length calculated is proportional to the flow rate. For a flow rate of 1.0 SLPM, the lengths for air and helium are 37 cm and 4.8 cm respectively. The lengths are directly proportional to flow rate so doubling the flow rate, for example, doubles the required tubing length. Though the flow rates through the system using helium may differ from that of air (due to viscosity differences) the same flow rate was used for each potential inert carrier.

**Table 3. Physical properties of Air and He**

	$k(\text{W/m-K})$	$c_p(\text{J/Kg-K})$	$\rho(\text{Kg/m}^3)$
Air	0.032	1000	1.2
He	0.17	5200	0.16

The constant pressure heat capacity of air was estimated from Appendix 15 and the thermal conductivity of air and He were taken from Appendix 12 of McCabe, et al.<sup>2</sup> The constant pressure heat capacity of He was taken from Appendix A of Reid, et al.<sup>3</sup> The temperature was taken to be 373 K for all physical properties.

#### 4.2 Temperature Gradients and Temperature Control.

In order for the idealized system discussed above to exist, there would have to be perfect (infinite) heat conduction within the jacket assembly and between the jacket and the bed assembly. The jacket and bed assembly of the system would also have to be perfectly insulated from its ambient temperature surroundings. The axial

---

<sup>3</sup> Reid, R.C., Prausnitz, J.M., and Poling, B.E., The Properties of Gases and Liquids, 4th ed., McGraw Hill, New York, NY, 1987.



temperature profile of the idealized system would be at ambient temperature outside of the jacket at the inlet end, at the set-point temperature within the jacket, and at ambient temperature outside the jacket at the outlet end. It would have the shape of a square wave.

For the real systems considered, 1/8" stainless steel tubing is used to direct the carrier into and through the jacketed region. The same tubing acts as a heat conductor within the jacket and as an insulator at the jacket's edges. Thus, if the set-point temperature is greater than room-temperature, the tubing entering the jacket will gradually change from room temperature, well outside the jacket, to a higher temperature, well inside the jacket. The temperature upstream of the sample container within the jacket is then not going to be uniform. The tubing exiting the system also gradually goes from the higher temperature well within the jacketed region to ambient temperature well outside. The temperature profile will be parabola shaped rather than shaped like a square wave.

Another important difference between the real and the idealized system is that the control provides for heat to be added in order to maintain the set-point temperature at the position of the control thermocouple. When the set-point temperature is greater than the ambient temperature and the vapor must be heated, the controller will heat part of the jacketed region to a temperature above the set-point temperature; that is, temperature gradients will be induced in order to heat incoming vapor to the set-point temperature. Temperature gradients may not only exist along the axis but radial gradients may also form. A temperature profile having a gradient in the axial direction and having a maximum (or minimum for cooling) upstream of the sample container allows the carrier to be heated (or cooled) quickly to the set-point temperature. This allows temperature gradients to be more gradual and prevents the formation of steep radial gradients within the sample container.

Another complicating factor is when the temperature at a point in the system depends on the temperature upstream there is a lag time which makes the temperature set-point difficult to maintain. The longer the heat exchanger the larger the lag time and the harder the system is to control. This is especially true when the system is subject to disturbances, for example, variations in flow rates. For this reason a long heat exchange section can cause problems, not only with regard to pressure drop, but also with respect to control.

Equation 10 can be used to make a rough estimate of the length of tubing required to heat vapor to a set-point, even when the temperature profile is parabola shaped. The tubing wall can be assumed to be a constant temperature above the set-point temperature upstream of the controlled point. For a parabolic temperature profile with a maximum about 4 C greater than the set-point temperature, for example, it may be assumed that the leading section of tubing is at a constant temperature of 2 C above the set-point temperature. In this case, the left side of Eq. 10 evaluates to  $2 \times 10^{-2}$  giving a

Graetz number of 3. When air is the inert carrier, the calculated length is reduced to 20 cm. Similarly the required length when He is used is also about half.

The length of the leading section of heated tubing largely determines the temperature gradient. The temperature is determined by the controller.

## 5. MODIFICATIONS MADE

### 5.1 Changes to Heat Exchanger Length.

The long coil of 1/8" tubing shown in Figure 2b is not present in the configuration shown in Figure 3b.

### 5.2 Changes Made to Reduce Axial Temperature Gradients.

Even though a small longitudinal gradient in temperature may be advantageous, too much curvature of the temperature profile is undesirable. It may result in a significant temperature gradient across the length of the sample container and not all of the adsorbent will be maintained at the same temperature. For this reason several features incorporated into the copper jacketed design are intended to reduce curvature of the temperature profile. These include increasing the length of the jacketed region and using copper (a good heat conductor) instead of glass as a sleeve material. Most heat is lost through the ends of the jacket. Therefore, the heating tape is wrapped more densely at the ends of the sleeve than at the middle so more heat is delivered where heat loss is greatest. The adsorption bed assembly incorporates "heat conductors." These put the assembly in intimate thermal contact with the copper sleeve. This allows heat to flow into the ends of the adsorption bed assembly as much as possible to reduce temperature gradients.

### 5.3 Stability to Flow Disturbances.

Not all of the innovations were directed towards reducing temperature gradients. When the system is running with the MB 41 pump, it is turned off before a gas sample for the GC is taken. This introduces a flow disturbance which causes temperature fluctuations. When the Ruska pump is used, flow through the temperature controlled region is greater when the piston rises and less when the piston falls. This may also cause temperature fluctuations.

For better temperature control, the thermal mass of the jacket had to be increased enough to make the system insensitive to these disturbances in carrier flow rate. The two concentric copper pipes and the tightly wrapped 3/8" copper coil provide for enhanced control stability.

## 6. TESTING MODIFICATIONS

The temperature control system was tested to determine the degree to which longitudinal temperature gradients develop. The role the heat conductors play in reducing these gradients and increasing control stability was determined. The stability of the system to flow disturbances was also measured. Three configurations were tested. Configuration 1 is the vertically oriented glass jacket. Configuration 2 is the vertically oriented copper jacketed design. A third configuration used the copper jacketed design but was oriented horizontally. Configuration 3 also lacked the rock wool insulation.

### 6.1 Measured Temperature Gradients Across the Sample Container.

The temperature at positions along the length of the adsorption bed was measured for various jacket designs. Temperature measurements were made by removing the bottom screen of the adsorbent sample container ( bed) and inserting a thermocouple (TC2) through the bed assembly fittings up to the flow inlet. The temperature was recorded and then the thermocouple was pulled down and read again. The control thermocouple (TC1) was taped to the outside of the adsorption bed for the Configuration 1 test. For the test of the Configuration 2, the control thermocouple was also taped to the outside of the bed. For the Configuration 3, the control thermocouple was placed between the 1" and the 3/4" copper tubing about 9" from the end of the assembly. The temperature set-points were 448 K for the Configuration 1 test, 423 K for the Configuration 2 test and 448 K for the Configuration 3 test. The results are shown in Figure 4. In the glass jacketed Configuration 1 ( $T_{SP} = 448$  K), the temperatures ranged from 461 K at the top of the sample container to 446 K at its bottom. For the copper jacketed Configuration 2 ( $T_{SP} = 423$  K), the measured temperature ranged from 424 K at the top of the bed to 421 K at the bottom. The temperature in Configuration 3 ( $T_{SP} = 448$  K) was 445 K throughout the bed.

### 6.2 Importance of Heat Conductor-Exchanger and Heat Conductor.

The importance of the copper sheathed stainless steel heat exchanger-conductor placed above the sample container and the aluminum foil heat conductor placed below the sample container of Configuration 2 was assessed by measuring the temperature response at the base of the sample container to a flow disturbance. The first measurements were taken on a system with an altered configuration where Tube A, the Heat Conductor-Exchanger and Tube B were replaced by a single section of 1/8" stainless steel tubing, and the aluminum foil Heat Conductor was removed. The second test was done with Configuration 2 unaltered. The temperature set-point for this test was 498.15 K. The control thermocouple was taped to the outside of the sample container. The measuring thermocouple was snaked up to the bottom of the sample container through the bottom section of 1/8" stainless steel tube. The first test system was thermally equilibrated with purge flow measuring on the flow meter at 0.7 SLPM and generating a

pressure of 27.78 psia at the pressure transducer. The second measurement was taken with the system thermal equilibrated without flow. Temperature readings for the first configuration are 501.69 K with flow and 499.17 K without flow. For the second configuration the corresponding temperature readings are 500.65 K and 500.52 K. The configuration incorporating heat conductors on either side therefore should be expected to provide for better temperature control than the configuration without heat conductors.

### 6.3 Measured Temperature Response to Flow Disturbance.

Configurations 1 and 2 were also tested to determine their response to a disturbance in flow. First the system was allowed to equilibrate with the MB 41 pump running. The temperature was recorded. Then the pump was turned off and after a short time the temperature was recorded again. For the glass jacketed Configuration 1 at a distance of 3.9 inches from the top of the 3 inch bed the temperature with flow was 443 K. When the MB 41 pump was stopped, the temperature at that point dropped to below 408 K. In contrast, when the same test was done with the copper jacketed Configuration 2 there was less than one degree difference between temperature measurements made with or without flow. Note that the temperature was measured almost one inch below the sample container. The axial temperature fluctuations the adsorbent would be subject to would be less than, though proportional, to the above.

The response of the vertical copper jacketed system (Configuration 2) to a flow disturbance was also tested by first setting the controller to 397 K and allowing the system to equilibrate overnight with the Ruska pump running on 25% power. The needle valve was set full open. The temperature was measured at a fixed location (at the bottom of the sample container) as a function of time by TC2. The pump was turned off immediately after the first measurement and was left off for 30 minutes. During this time the temperature dropped from 399.6 K to 399.4 K or about 0.2 K. The pump was then restarted at 25 % power and was left on. The temperature then rose to 399.47 K, dropped to 399.45 K and then rose to 399.58 K before beginning the drop again. The error these fluctuations with time might cause in concentration measurements was estimated by taking the standard deviation of the temperature measurements, which was 0.07 K, and multiplying it by values in tables 1 and 2. The results are shown in Table 3 and Table 4.

**TABLE 4. Percent error in  $p$  per standard deviation of  $T$  with vertical copper (R-134a/BPL)**

$T$	$\theta = 0.5$	$\theta = 0.1$	$\theta = 0.01$	$\theta = 0.001$	$\theta = 0.0001$
25 C	0.0084%	0.1512%	0.3878%	0.5005%	0.5649%
50 C	0.0028%	0.0504%	0.1799%	0.2667%	0.3003%
150 C	0.0000%	0.0014%	0.0028%	0.0028%	0.0021%

**TABLE 5. Percent error in  $p$  per standard deviation of  $T$  with vertical copper (Toluene/BPL)**

<b>T</b>	<b><math>\theta = 0.5</math></b>	<b><math>\theta = 0.1</math></b>	<b><math>\theta = 0.01</math></b>	<b><math>\theta = 0.001</math></b>	<b><math>\theta = 0.0001</math></b>
<b>25 C</b>	0.5362%	0.7007%	0.8414%	0.9499%	1.0409%
<b>50 C</b>	0.4144%	0.5880%	0.7077%	0.8001%	0.8771%
<b>150 C</b>	0.0287%	0.2709%	0.3913%	0.4501%	0.4963%

## 7. DISCUSSION

Ideally, when measuring an adsorption isotherm, the temperature of the adsorbent and the vapor in contact with the adsorbent is maintained at a constant known temperature. However, devices used to measure temperature have limited accuracy. Even if the thermocouples and supporting electronics are perfectly accurate, temperatures may vary from point to point in the sample container or the temperatures of the adsorbent and the surrounding vapor may differ. Temperature variations and errors in temperature measurement prevent the temperature of the adsorbent sample from being known. The temperature at a single point will also vary with time, that is, temperature controllers also have limitations. Temperature variations in time due to limitations of the temperature control approach prevent the system from ever reaching thermodynamic equilibrium.

Concentrations are determined by taking a small sample of vapor from the system and directing it to a gas chromatograph. The GC measures mass (or moles) so the volume of the injection loop must be known to determine the concentration. If the temperature and pressure (actually the ratio  $T/p$ ) is the same throughout the system, the concentration of the gas in the injection loop is the same as that in the bypass loop. Errors in concentration determination can be due to differences in  $T/p$  between the injection loop and the rest of the system. In the challenge mode, the sample container and heat exchange assembly is maintained at the isotherm temperature rather than the ballast temperature. Therefore, the condition just discussed is not maintained. The error this introduces is dependent on the ratio of the volume of the ballast and the volume in the jacketed region. With a large enough ballast the error is insignificant. More significant is the situation when temperatures or pressures in the injection loop and the ballast differ.

The volumetric system determines the amount adsorbed by taking the difference between the vapor-phase concentration in bypass mode and the vapor-phase concentration in the challenge mode at equilibrium. This value is then multiplied by the system volume and divided by the adsorbent sample weight in order to obtain the change in adsorbed-phase concentration. The change in adsorbed-phase concentration is added to that determined on the previous point.

Equations 10 and 11 may also be used to estimate the length of tubing required to heat incoming gas for real systems from the temperature measurements reported above. In order to do so, a tentative simplifying assumption has to be made. In Configuration 1 the temperature at the top of the bed was 461 K. Tentatively assuming that this is the temperature of the leading heat exchange section, Eq. 10 gives  $Gz = 4.5$  and with a 1.0 SLPM flow rate. The required heat exchange length would then be 14 cm (or 5-1/2 inches). The coil of configuration 1 is several feet long. This implies that only a short section of it is heated to or above 461 K. This can occur when the heat conduction between the jacket and the heat exchange tubing is poor. For Configuration 2 operated under the same conditions (except the  $T_{sp} = 423$  K)  $Gz = 3.1$  and the required heat exchange length would be 21 cm (or 8 inches). This length is much closer to its real length. This implies that the assumptions made in order to perform the calculation are closer to the actual state of the system. The lateral temperature gradient is less steep because the heat exchange tubing is in better thermal contact with the jacket. In Configuration 3, there was no temperature gradient along the flow path upstream of the sample container. In this configuration radial temperature gradients may form. Note that the control thermocouple was placed between the 3/4" and the 1" copper pipes. The temperature set-point was 448 K but the measurement thermocouple placed at the base of the sample container read 445 K. Configuration 3 was not insulated. There was more heat loss radially than axially and therefore the radial rather than an axial gradient should be expected. This configuration needs to be tested with insulation to determine whether the horizontal orientation has superior temperature control to the vertical orientation. One advantage of a horizontal orientation should be improved temperature stability due to the reduction in natural convection currents. (Regardless of the temperature control properties of the horizontal orientation, this orientation makes it easier to change adsorbent.)

## 8. CONCLUSION

Changing from glass to copper as the main material of construction increased the system durability, improved temperature control, increased the temperature range over which measurements can be made, and reduced the cost of construction.

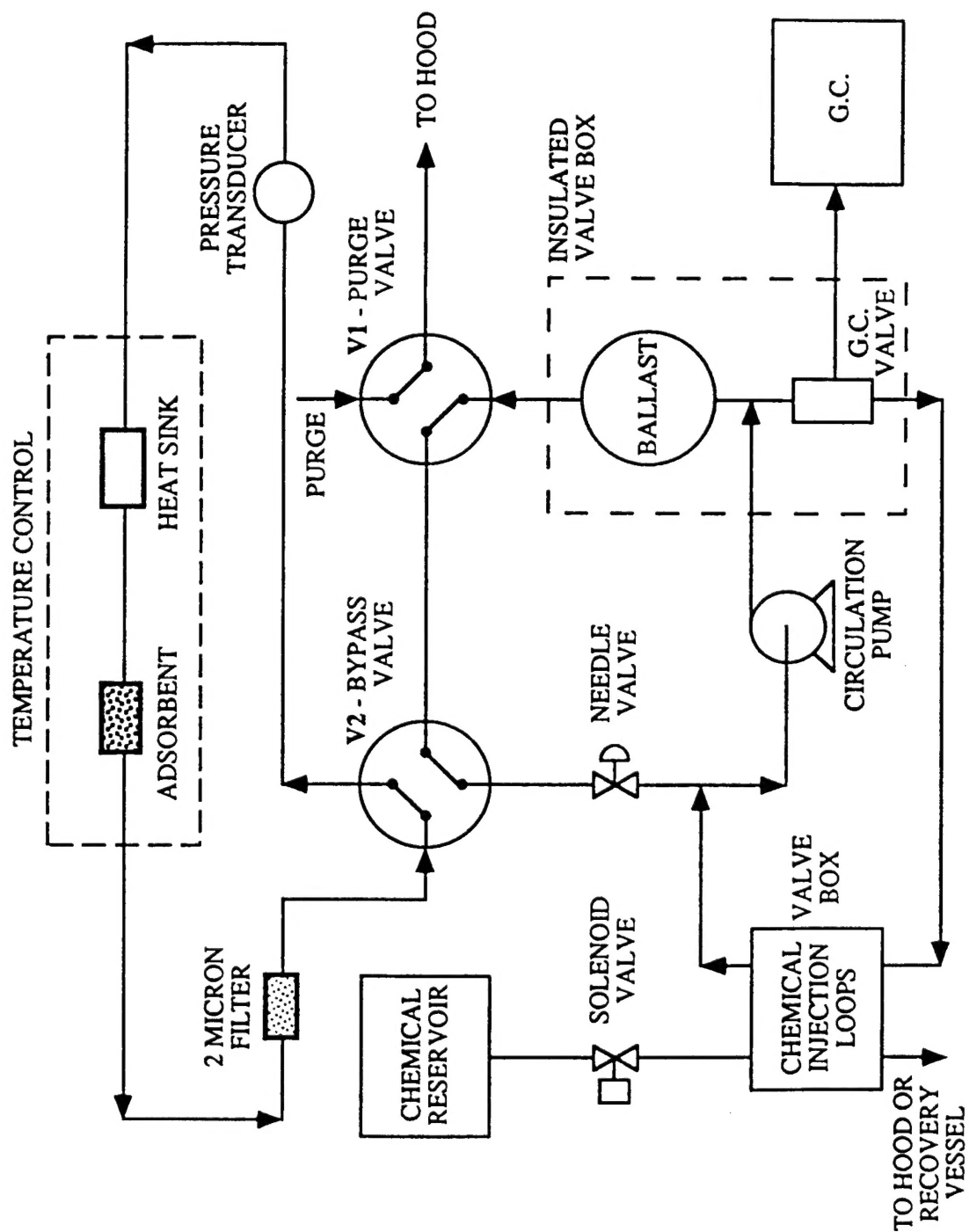
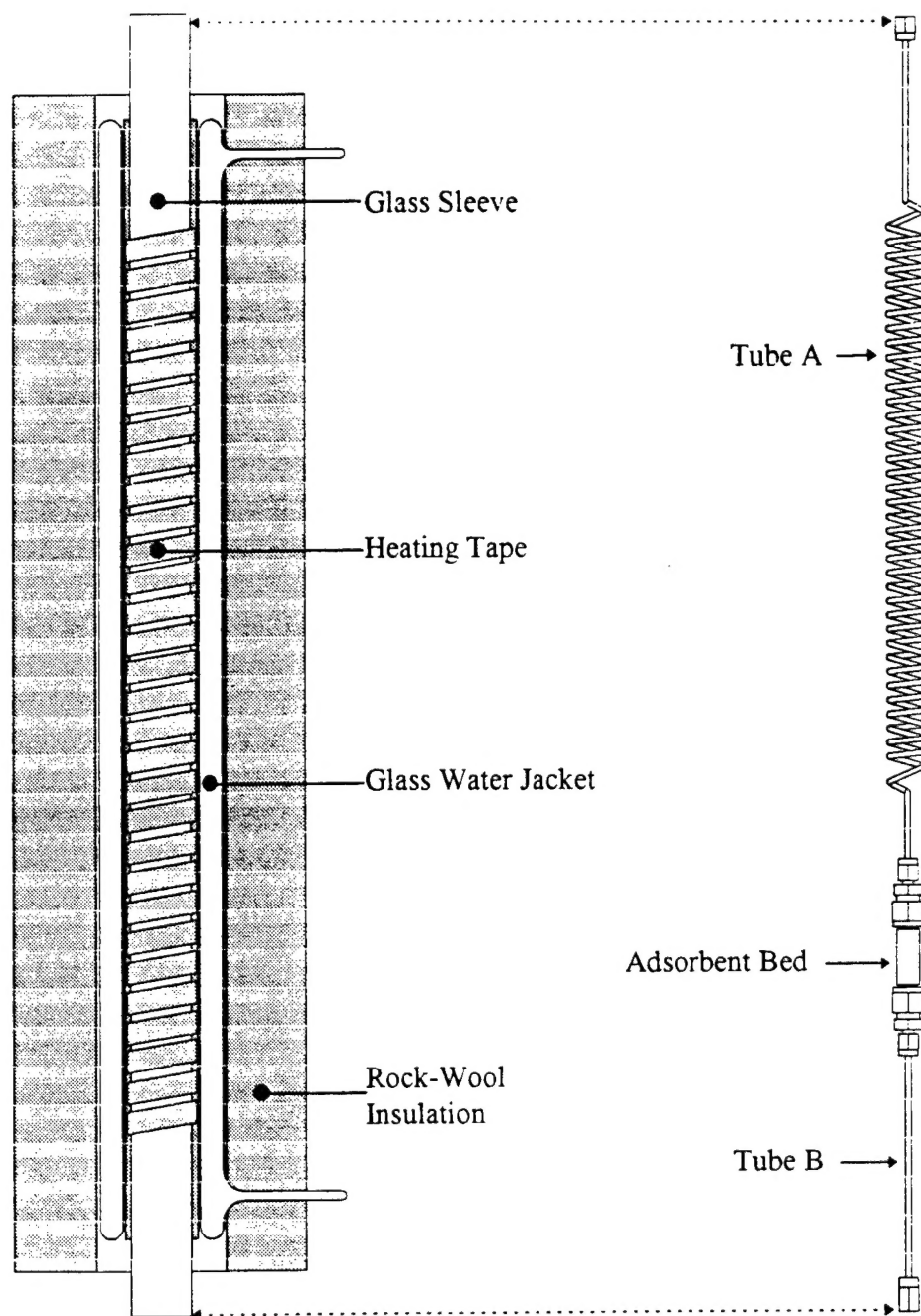


FIGURE 1. Volumetric Isotherm System Schematic

a) Old Temperature Control System

b) Old Adsorption Bed



**FIGURE 2.** a) Old Temperature Control System and b) Old Adsorption Bed Schematics



a) Temperature Control Jacket

b) Adsorption Bed Assembly

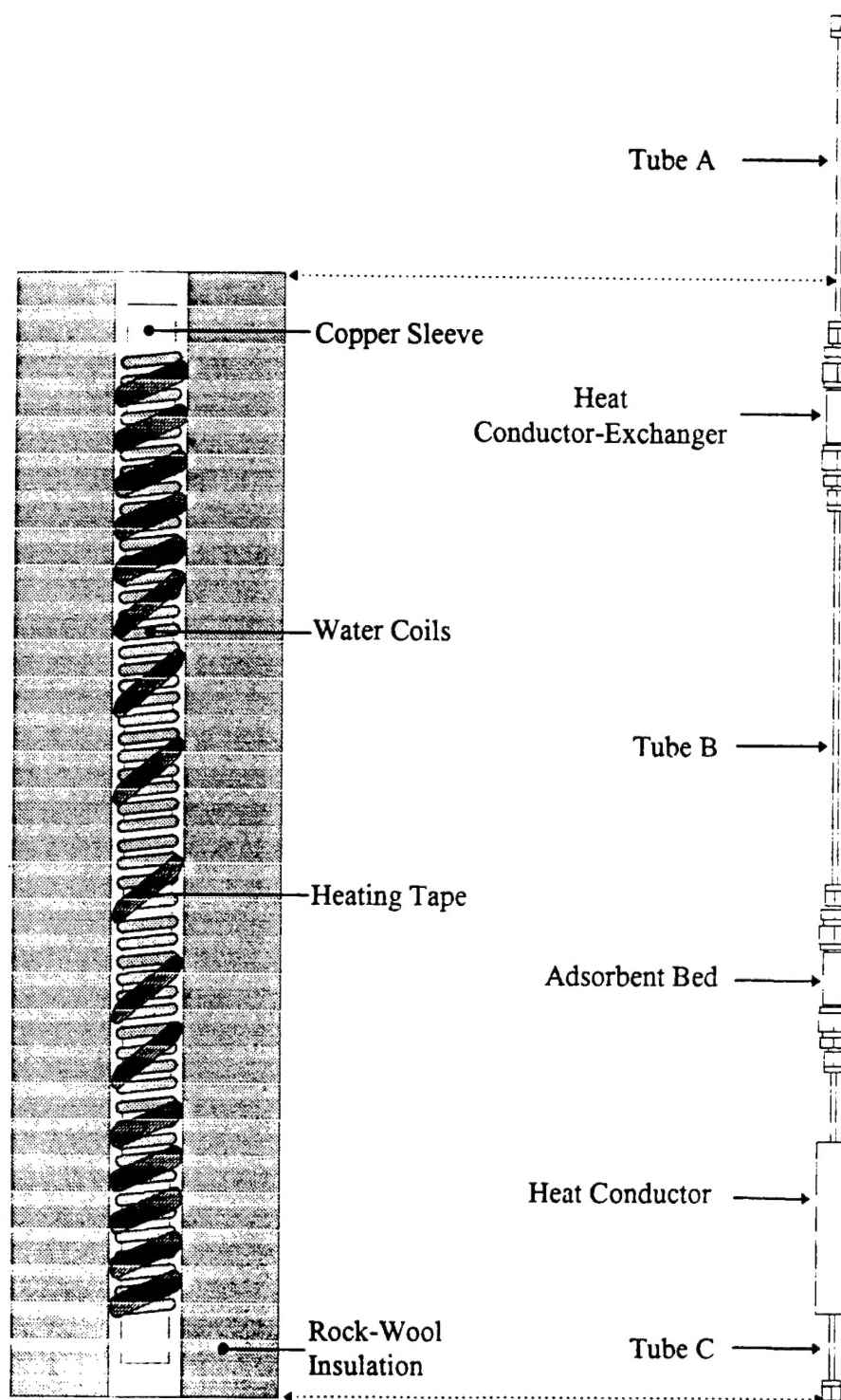
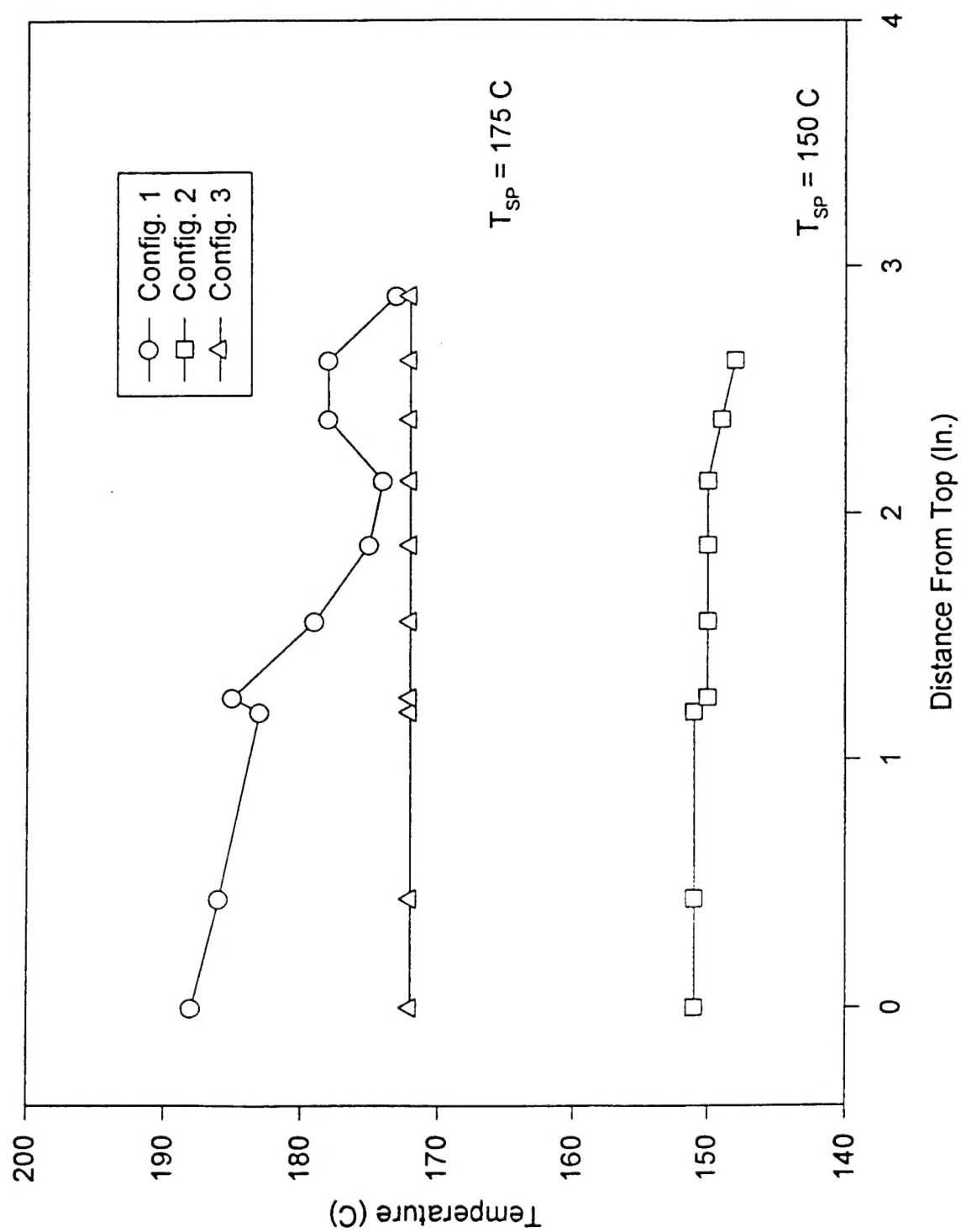


FIGURE 3. a) Temperature Control Jacket and b) Adsorption Bed Assembly Schematics



**FIGURE 4.** Temperature Gradient Across Adsorbent Sample Container